

(19) World Intellectual Property
Organization
International Bureau



Revised PCT/PTO 23 FEB 2005
10/525611

(43) International Publication Date
11 March 2004 (11.03.2004)

PCT

(10) International Publication Number
WO 2004/020686 A3

(51) International Patent Classification⁷: C23C 14/28,
C30B 29/16, C23C 14/08, H01L 29/205, 29/267, C30B
23/02

(21) International Application Number:
PCT/US2003/027143

(22) International Filing Date: 27 August 2003 (27.08.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/406,500 28 August 2002 (28.08.2002) US

(71) Applicant (*for all designated States except US*): MOX-
TRONICS, INC. [US/US]; 504 N. Village Circle, Colum-
bia, MO 65203 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): WHITE, Henry, W.
[US/US]; 2814 Wild Plum Court, Columbia, MO 65201
(US). RYU, Yungryel [KR/US]; 504 N. Village Circle, Co-
lumbia, MO 65203 (US). LEE, Tae-Seok [KR/US]; 2476
Warm Springs Lane, Naperville, IL 60564 (US).

(74) Agent: JACOBS, David; Gesmer Updegrave LLP, 40
Broad Street, Boston, MA 02109 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

(88) Date of publication of the international search report:
14 October 2004

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: A HYBRID BEAM DEPOSITION SYSTEM AND METHODS FOR FABRICATING ZNO FILMS, P-TYPE ZNO FILMS, AND ZNO-BASED II-VI COMPOUND SEMICONDUCTOR DEVICES

(57) Abstract: A hybrid beam deposition (HBD) system and methods according to the present invention utilizes a unique combination of pulsed laser deposition (PLD) technique and equipment with equipment and techniques that provide a radical oxygen rf-plasma stream to effectively increase the flux density of available reactive oxygen at a deposition substrate for the effective synthesis of metal oxide thin films. The HBD system and methods of the present invention further integrate molecular beam epitaxy (MBE) and/or chemical vapor deposition (CVD) techniques and equipment in combination with the PLD equipment and technique and the radical oxygen rf-plasma stream to provide elemental source materials for the synthesis of undoped and/or doped metal oxide thin films as well as the synthesis of undoped and/or doped metal-based oxide alloy thin films.

WO 2004/020686 A3

INTERNATIONAL SEARCH REPORT

PCT/US 03/27143

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C14/28 C30B29/16 C23C14/08 H01L29/205 H01L29/267
C30B23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C C30B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 046 464 A (SCHETZINA JAN FREDERICK) 4 April 2000 (2000-04-04)	1-8
Y	*column 6, lines 21-28; column 16, lines 50-57; column 18, line 37 to column 19, line 20*claims 1-30	19-26, 44-67
X	EP 1 054 082 A (STANLEY ELECTRIC CO LTD ;YAO TAKAFUMI (JP)) 22 November 2000 (2000-11-22) *column 3, lines 36-58; column 4, lines 28-33*	1-8



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the International filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the International search

27 July 2004

Date of mailing of the International search report

23.08.04

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Boussard, N

INTERNATIONAL SEARCH REPORT

PCT/US 03/27143

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	H.J. KO, Y.F. CHEN, Z. ZHU, T. YAO: "Photoluminescence properties of ZnO epilayers grown on CaF ₂ (111) by plasma assisted molecular beam epitaxy" APPLIED PHYSICS LETTERS, vol. 76, no. 14, 3 April 2000 (2000-04-03), pages 1905-1907, XP000950583 page 1905	1-8
X,P	Y.R. RYU: "Properties of arsenic-doped p-type ZnO grown by hybrid beam deposition" APPLIED PHYSICS LETTERS, vol. 83, no. 1, 7 July 2003 (2003-07-07), pages 87-89, XP002273918 the whole document	1-8
A	RYU Y R ET AL: "Synthesis of p-type ZnO films" JOURNAL OF CRYSTAL GROWTH, NORTH-HOLLAND PUBLISHING CO. AMSTERDAM, NL, vol. 216, no. 1-4, June 2000 (2000-06), pages 330-334, XP004206254 ISSN: 0022-0248 page 331	1-8
X	KUMANO H ET AL: "Luminescence properties of ZnO films grown on GaAs substrates by molecular-beam epitaxy excited by electron-cyclotron resonance oxygen plasma" JOURNAL OF CRYSTAL GROWTH, NORTH-HOLLAND PUBLISHING CO. AMSTERDAM, NL, vol. 214-215, June 2000 (2000-06), pages 280-283, XP004201009 ISSN: 0022-0248	9-18
Y	the whole document	19-26
X	US 2001/036214 A1 (LOGVENOV GENNADI ET AL) 1 November 2001 (2001-11-01) page 3, paragraph 46 - page 4, paragraph 64	9-18
X	GARCA LOPEZ J ET AL: "Role of the oxygen plasma during in situ growth of YBa ₂ Cu ₃ O _{6+x} thin films by pulsed laser deposition" PHYSICA C, NORTH-HOLLAND PUBLISHING, AMSTERDAM, NL, vol. 307, no. 3-4, October 1998 (1998-10), pages 298-306, XP004150009 ISSN: 0921-4534 paragraphs '0001!, '0002!	9-18
	-/-	

INTERNATIONAL SEARCH REPORT

PCT/US 03/27143

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	TSURUMI T ET AL: "ELECTRIC PROPERTIES OF ZINC OXIDE EPITAXIAL FILMS GROWN BY ION-BEAM SPUTTERING WITH OXYGEN-RADICAL IRRADIATION" JAPANESE JOURNAL OF APPLIED PHYSICS, PUBLICATION OFFICE JAPANESE JOURNAL OF APPLIED PHYSICS. TOKYO, JP, vol. 38, no. 6A, June 1999 (1999-06), pages 3682-3688, XP000883343 ISSN: 0021-4922	27-43
Y	paragraphs '0001!, '0002!, '03.2!	44-108
Y	EP 1 081 256 A (STANLEY ELECTRIC CO LTD ; YAO TAKAFUMI (JP)) 7 March 2001 (2001-03-07) the whole document	68-108
A	RYU Y R ET AL: "Fabrication of homostructural ZnO p-n junctions" JOURNAL OF CRYSTAL GROWTH, NORTH-HOLLAND PUBLISHING CO. AMSTERDAM, NL, vol. 219, no. 4, 1 November 2000 (2000-11-01), pages 419-422, XP004219184 ISSN: 0022-0248 the whole document	68-108
X	US 5 849 630 A (JOHNSON DAVID A) 15 December 1998 (1998-12-15) column 2, lines 31-63	109-117
X	EP 0 591 607 A (MITSUBISHI ELECTRIC CORP) 13 April 1994 (1994-04-13) column 5, line 30 - column 6, line 42	109-117

INTERNATIONAL SEARCH REPORT

international application No.
PCT/US 03/27143

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8

Claims 1 to 8 are related to an hybrid beam deposition apparatus for synthesizing metal oxide (doped and/or alloys) films based on the combination of an oxygen rf plasma source subsystem and a metal oxide plasma generating subsystem.

2. claims: 9-26

Claims 9 to 26 are related to an hybrid beam deposition method for synthesizing metal oxide and metal-based oxide alloy films based on the combination of an oxygen rf plasma pre- and post-treatment and a metal oxide plasma.

3. claims: 27-67

Claims 27 to 67 are related to an hybrid beam deposition method for synthesizing doped metal oxide and metal-based oxide alloy films based on the combination of an oxygen rf plasma, a metal oxide plasma and a dopant material stream.

4. claims: 68-108

Claims 68 to 108 are related to an hybrid beam deposition method for fabricating a semiconductor device based on the combination of an oxygen rf plasma, a metal oxide plasma, a dopant and an elemental material stream.

5. claims: 109-117

Claims 109 to 117 are related to a method for adhering bilayered ohmic contacts to a semiconducting composite structure to form a semiconductor device.

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/US 03/27143

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6046464	A	04-04-2000	US 5670798 A	23-09-1997
			AT 245851 T	15-08-2003
			AU 5374296 A	16-10-1996
			DE 69629183 D1	28-08-2003
			DE 69629183 T2	15-04-2004
			EP 0818056 A2	14-01-1998
			WO 9630945 A2	03-10-1996
			US 5679965 A	21-10-1997
EP 1054082	A	22-11-2000	JP 3492551 B2	03-02-2004
			JP 2000332296 A	30-11-2000
			DE 60008960 D1	22-04-2004
			EP 1054082 A1	22-11-2000
			US 6407405 B1	18-06-2002
US 2001036214	A1	01-11-2001	WO 0155472 A2	02-08-2001
EP 1081256	A	07-03-2001	JP 3424814 B2	07-07-2003
			JP 2001068485 A	16-03-2001
			EP 1081256 A2	07-03-2001
			US 6664565 B1	16-12-2003
US 5849630	A	15-12-1998	US 5144410 A	01-09-1992
EP 0591607	A	13-04-1994	JP 6061269 A	04-03-1994
			EP 0591607 A2	13-04-1994
			US 5483089 A	09-01-1996